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OPTIMUM PRODUCTION OF ATOMIC OXYGEN FOR USE IN ANALYTICAL TECHNOLOGY

Dale J. Milnes, et al

Ozone Research and Equipment Corporation

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Optimum Production of Atomic Oxygen for Use in Analytical Technology

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16. Abstracts

A project was undertaken to investigate the feasibility of generating atomic oxygen by chemically induced catalytic decomposition of ozone at near ambient temperatures. The scope of this work was to perform a complete literature survey to discover chemicals known to decompose ozone and then to introduce these into a linear analytical set-up in which operating parameters could be varied to establish optimum production of atomic oxygen as a function of ozone decomposition. The report consists of eight sections in which the following information is presented: Literature Research - a list of selected references are given; Results of Literature Research - presents chemicals selected as candidates for the decomposition of ozone and presents data confirmed by survey: Initial Experimentation; Analysis of Initial Experimentation; Final Experimentation; and Conclusions.

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Optimum Production of Atomic Oxygen for Use in Analytical Technology

by

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Contract No. 68-02-0558
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Prepared for

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U. S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

March 1973

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SECTION I. PURPOSE AND SCOPE

The purpose of this contract has been to investigate the feasibility of generating atomic oxygen by chemically induced catalytic decomposition of ozone at near ambient temperatures. The scope has been to perform a complete literature survey to discover chemicals known to decompose ozone and then to introduce these into a linear analytical set up in which operating parameters could be varied to establish optimum production of atomic oxygen as a function of ozone decomposition.

SECTION II. BACKGROUND

It is well known that at high temperatures, 1832°F, ozone decomposes to atomic oxygen and, at very low pressures of less than 10 torr, atomic oxygen exists for a sufficient time interval to be measured by the reaction $NO_2 + O \rightarrow NO + O_2$; $NO + O \rightarrow NO_2 + h\nu$. This reaction is accompanied by measurable light emission, the magnitude of which is a function of gas concentrations. The reaction has been exploited in experimental techniques for the determination of NO_x concentrations by back titration of O to determine NO. However, the technique is debilitated in two respects by dependence upon high temperature: first, precision apparatus is required to achieve and reasonably stabilize the required high temperature in a reaction chamber. Second, light emission must be measured

significantly downstream of the high temperature reaction chamber due to interfering radiation from the chamber itself; thus, the light intensity measurement is at a locale where the magnitude of the reaction light intensity is below maximum.

It is known that at ambient temperatures a stream of $O_3 + O_2$ can be passed through beds of certain materials or chemicals, that downstream measurements establish no ozone is present in the effluent gas, and that there is no chemical change in the bed material. These materials can be categorized as catalysts, adsorbents, and catalyst-adsorbents of ozone.

Ozone is an unstable chemical that decomposes to oxygen at ambient temperatures, the rate being a function of temperature, pressure and what might be called the container effect. When a certain activation energy is supplied, the ozone molecule decomposes. A change in temperature or pressure increases the collision rate of molecules with each other and with the container walls and collisions provide the activation energy for decomposition. Various materials sensitize to varying degrees the decomposition rate and those which do so to a very high degree are in effect decomposition catalysts. Catalysts such as Hopcalite and Iron Oxide probably involve an even exchange of oxygen atoms between ozone and the catalyst but, upon reformation of the oxygen atoms, molecular oxygen (O_2) rather than triatomic oxygen (O_3) is formed.

Decomposition of ozone is accompanied by the liberation of the heat of ozone formation. At high ozone concentrations (30%-40% by weight) the liberated heat of formation is sufficient to provide activation energy for the decomposition of surrounding molecules resulting in a self-sustaining decomposition of ozone. The liberated heat of adsorption of ozone provides sufficient activation energy for decomposition of ozone as an attendant to adsorption, e.g., adsorption in active carbon is accompanied by decomposition.

In view, therefore, of the fact that ozone does decompose to O_2, there is the reasonable expectation that 0 exists for an interval of time. The decomposition reaction would appear limited to (a) $2O_3 \rightarrow 2O + 2O_2 \rightarrow 3O_2$ or (b) $2O_3 \rightarrow 6O \rightarrow 3O_2$. In either case 0 exists for an interval. If, in the case of catalytic decomposition to molecular oxygen, an even interchange of oxygen atoms occurs between ozone and the catalyst, then the reactions would appear similarly limited and again atomic oxygen would exist for an interval of time.

A. $O_3 + RO \rightarrow RO + O + O_2$

B. $O_3 + RO_2 \rightarrow RO_2 + O + O_2$

C. $O_3 + RO_3 \rightarrow RO_3 + O + O_2$

The contract effort, therefore, has been directed toward discovering materials which significantly accelerate the decomposition of ozone at ambient temperatures and ascertain if the time interval during which atomic oxygen persists in

the presence of such a material is sufficient for the reaction NO_x + 0 to be favorable over 0 + 0, or at least to be sufficiently competitive to provide a measurable NO_x + 0 reaction within reasonable instrumentation standards. It has been so established that attendant to high temperature decomposition the time interval that 0 persists is adequate and the NO_x + 0 reaction is competitive. The contract effort further intended to optimize the reaction by investigating the consequence of changing experimental parameters: temperature and pressure over a moderate span, system geometry, flow rates, etc.

SECTION III. LITERATURE RESEARCH

An extensive literature survey was proceeded upon to discover candidate chemicals for the decomposition of ozone. Subsidiary research was performed to achieve familiarity with the experiences, instrumentation, and circumstances attendant to prior investigations into atomic oxygen production and atomic oxygen-NO_x reactions.

The following selected references were studied and would be recommended as a bibliography for researchers in this area:

Bartz, J. A. and J. J. Vidal, "Catalytic Oxygen Atom Probe for Determining Concentration in High Temperature High Velocity," U. S. Clearinghouse Federal Scientific Technical Information, AD 1970, No. 704814 1970.

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Reeves, R. R., P. Harteck, and Mannella, "Rate of Recombination of Oxygen Atoms," Journal of Chemical Physics, Vol. 32, p. 632, 1960.

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SECTION IV. RESULTS OF LITERATURE RESEARCH

As a consequence of a survey of the literature plus in-house (Ozone Research & Equipment Corporation) experience with ozone decomposition, the following chemicals were selected as candidates for the decomposition of ozone:

A. Molecular Sieve: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \times H_2O$

B. Hopcalite: MnO_2, CuO, CoO, and Ag_2O

C. Silica Gel: SiO_2

D. Activated Charcoal: C

E. Soda Lime: NaOH and CaO

F. Nickel: Ni

G. Iron Oxide: Fe_2O_3

H. Manganese Dioxide: MnO_2

I. Sodium Hydroxide: NaOH

J. Calcium Metasilicate: $CaSiO_3$

K. Sodium Metasilicate: Na_2SiO_3

L. Vanadium Pentoxide: V_2O_5

The literature survey established and/or confirmed the following significant data:

A. The substances which catalytically decompose ozone are mainly oxides of metal.

B. There has been no determination of the intermediate product, atomic oxygen, attendant to the decomposition of ozone to oxygen.

C. There has been no study on the feasibility of generating atomic oxygen from the catalytic decomposition of ozone by substances at or near ambient temperatures.

D. The principle of atomic oxygen measurement using NO_2 is well established. The reaction $NO + O \rightarrow NO_2 + h\nu$ provides a measurable yellow-green glow, the intensity of which varies as a function of concentration.

E. In the cited reaction, maximum light intensity occurs when the concentration of NO_2 is equal to one-half the concentration of atomic oxygen.

F. In the cited reaction, the light is extinguished when the NO_2 concentration equals the atomic oxygen concentration.

G. The measurement instrumentation is critical and the work of Kaufman* provides the best data for model construction.

*Reference Cited.

H. The Kaufman technique provides the following principles and parameters:

1. Vacuum in the one torr range is required.

2. A photometer sensitive in the 5500Å region is required.

3. Precision measurement of gas flows are required.

4. Because of the extremely low gas flows, a manometer measured pressure drop across precision bore capillaries is essential to gas flow measurement.

5. Determination of capillary size may be established using Poiseuille's Law of Gases which is expressed:

$$F = \frac{\pi r^4 (P_1^2 - P_2^2)}{16 \eta L R T}$$

Where F = molar flow rate, gmole/sec

r = radius of capillary, cm

P_1 = pressure at inlet of capillary, dynes/cm^2

P_2 = pressure at outlet of capillary, dynes/cm^2

η = viscosity of gas, g/cm-sec

L = length of capillary, cm

R = gas law constant, $\frac{cm^3\text{-dynes/}cm^2}{\text{gmole-}^\circ K}$

T = temperature of gas, °K

SECTION V. INITIAL EXPERIMENTATION

Initial experimentation was conducted using an analytical set up as illustrated in Figure I. A total of 72 tests were conducted upon the above cited candidate chemicals and the results were entirely negative, that is, the photometric equipment provided a zero light signal indication in every test.

A number of parameters were varied during these tests:

A. Tests were conducted at both 75° and 200°F.

B. Three different reaction vessels were employed having the following dimensions:

1. 8 mm ID x 6 mm long

2. 3 mm ID x 20 mm long

3. 8 mm ID x 25 mm long

C. The oxygen-ozone stream of 20-60 cc/min at 1 torr and the NO_2 stream of .12-.36 cc/min at 1 torr were presented in alternative manners.

1. The oxygen-ozone stream was passed through the catalytic chemical bed and immediately upon exiting the NO_2 stream was impinged upon it.

2. The oxygen-ozone stream and the NO_2 stream were joined before entering the catalytic chemical bed.

SECTION VI. ANALYSIS OF INITIAL EXPERIMENTATION

It was concluded, upon analysis, that the negative results of initial experimentation could be attributed to one or more of the following:

A. An atomic oxygen yield does not occur as an attendant to the catalytic decomposition of ozone at near ambient temperatures.

B. The existance interval of atomic oxygen generated by catalytic decomposition of ozone at or near ambient temperatures is not adequate for the $NO_x + 0$ reactions to occur.

C. At near ambient temperatures the reaction $0 + 0 \rightarrow O_2$ is preponderantly more favorable than the reactions $NO_x + 0$.

D. The photometric instrumentation employed was not adequately sensitive to respond to the emitted reaction light signal.

A meeting was held at the facility of the Contractor between project personnel and representatives of the Environmental Protection Agency: Mr. John E. Sigsby, Project Officer, and Mr. Frank Black, subsequent Project Officer. An in depth analysis of instrumentation and the experimental set up provided the following conclusions and recommendations:

A. A more sensitive photometric circuit and components would be required to establish the certainty of the negative results.

B. Recommended improvements in high vacuum system techniques would enhance the possibility of positive results.

C. High flows of low concentrations NO_2 (100 ppm) rather than low flows of high concentrations NO_2 (100%) as had been employed in the initial experiments would both enhance the possibility of positive results and be more equatable with existing data on thermal decompositior of ozone.

Subsequently to this meeting, the Contractor was provided on loan from the Environmental Protection Agency the following more sensitive photometric equipment:

A. RCA Type 7265 Photomultiplier tube

B. Keithley Model 414S Picoammeter

C. Keithley Model 245 High Voltage Supply

SECTION VII. FINAL EXPERIMENTATION

A. Instrumentation and Set Up

Figure II is a perspective drawing of the experimental set up for the determination and measurement of atomic oxygen. Figure III is a block diagram of this set up. Figure IV is a drawing of the reaction vessel.

In operation, the motive force for the flow of gases is the vacuum pump, providing a vacuum of .5 to 3 torr in the reaction vessel. Candidate chemicals were charged into one or the other of the two catalytic chambers illustrated in Figure IV. A 2%/wt. concentration of ozone in an 11 cc/min (STP) oxygen stream passed from the ozonator through the catalytic chamber and impinged upon the glass window in the immediate view of the photomultiplier tube. Simultaneously a 100 ppm/volume NO_2 concentration in a 0-28 cc/min (STP) argon stream impinged adjacently upon the window. The generation of atomic oxygen by the catalytic decomposition of ozone is sensed and measured by the photometer responding to the ultimate reaction of $NO_2 + O \rightarrow NO + O_2$; $NO + O \rightarrow NO_2 + h\nu$. To establish the facility and accuracy of the experimental set up, a signal was deliberately generated by introducing $NO + O_3$ to produce the reaction $NO + O_3 \rightarrow NO_2 + O_2 + h\nu$. This photometry responded quite sensitively to this reaction.

B. Final Experimental Results and Data

A total of 24 test schedules were conducted as set forth in Figure V. Each candidate chemical was charged into the teflon catalytic chamber (Figure IV Detail B) and the experiment conducted at 75°F. Each candidate chemical was then charged successively into the ceramic catalytic chamber (Figure IV Detail A) and the experiment conducted over the temperature span of 75°F to 380°F proceeding over a 15 minute interval.

The light signal was zero in the instance of every candidate chemical under every test condition.

SECTION VIII. CONCLUSIONS

Ozone can be catalytically decomposed to molecular oxygen at ambient temperatures by certain selected chemicals, predominantly oxides of metals. The existance of the intermediate product, atomic oxygen, is a persuasive deduction that has neither been proved nor controverted by this contract effort.

It is concluded that any atomic oxygen generated as an intermediate product in the catalytic decomposition of ozone does not at ambient temperatures provide the following reaction: $NO_2 + O \rightarrow NO + O_2$; $NO + O \rightarrow NO_2 + h\nu$.

It is theorized that the reaction of oxygen atoms to combine as oxygen molecules proceeds to the exclusion of atomic oxygen reactions with oxides of nitrogen at ambient temperatures.

It is recognized that the extensive surface area of the catalysts may enhance the molecular oxygen reaction.

FIGURE V
Test Schedule

Test No.	Chemical	Temp °F	Ozone Flow 2% O_3/wt (STP)	Nitrogen Dioxide Flow 100 ppm NO_2 in Argon (STP)	Signal
1	Molecular Sieve	75°F	11 cc/min	0-28 cc/min	Zero
2	Hopcalite	75°F	11 cc/min	0-28 cc/min	Zero
3	Silica Gel	75°F	11 cc/min	0-28 cc/min	Zero
4	Charcoal	75°F	11 cc/min	0-28 cc/min	Zero
5	Soda Lime	75°F	11 cc/min	0-28 cc/min	Zero
6	Nickel	75°F	11 cc/min	0-28 cc/min	Zero
7	Iron Oxide	75°F	11 cc/min	0-28 cc/min	Zero
8	Manganese Dioxide	75°F	11 cc/min	0-28 cc/min	Zero
9	Sodium Metasilicate	75°F	11 cc/min	0-28 cc/min	Zero
10	Calcium Metasilicate	75°F	11 cc/min	0-28 cc/min	Zero
11	Sodium Hydroxide	75°F	11 cc/min	0-28 cc/min	Zero
12	Vanadium Pentoxide	75°F	11 cc/min	0-28 cc/min	Zero
13	Molecular Sieve	75°F-380°F	11 cc/min	0-28 cc/min	Zero
14	Hopcalite	75°F-380°F	11 cc/min	0-28 cc/min	Zero
15	Silica Gel	75°F-380°F	11 cc/min	0-28 cc/min	Zero
16	Charcoal	75°F-380°F	11 cc/min	0-28 cc/min	Zero

Test No.	Chemical	Temp °F	Ozone Flow 2% 03/wt (STP)	Nitrogen Dioxide Flow 100 ppm NO_2 in Argon (STP)	Signal
17	Soda Lime	75°F-380°F	11 cc/min	0-28 cc/min	Zero
18	Nickel	75°F-380°F	11 cc/min	0-28 cc/min	Zero
19	Iron Oxide	75°F-380°F	11 cc/min	0-28 cc/min	Zero
20	Manganese Dioxide	75°F-380°F	11 cc/min	0-28 cc/min	Zero
21	Sodium Metasilicate	75°F-380°F	11 cc/min	0-28 cc/min	Zero
22	Calcium Metasilicate	75°F-380°F	11 cc/min	0-28 cc/min	Zero
23	Sodium Hydroxide	75°F-380°F	11 cc/min	0-28 cc/min	Zero
24	Vanadium Pentoxide	75°F-380°F	11 cc/min	0-28 cc/min	Zero

Molecular Sieve: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \times H_2O$
Silica Gel: SiO_2
Charcoal: C
Soda Lime: NaOH and CaO
Iron Oxide: Fe_2O_3
Manganese Dioxide: MnO_2
Nickel: Ni
Sodium Metasilicate: Na_2SiO_3
Calcium Metasilicate: $CaSiO_3$
Sodium Hydroxide: NaOH
Hopcalite: Mixture of MnO_2, CuO, CoO, and Ag_2O
Vanadium Pentoxide: V_2O_5

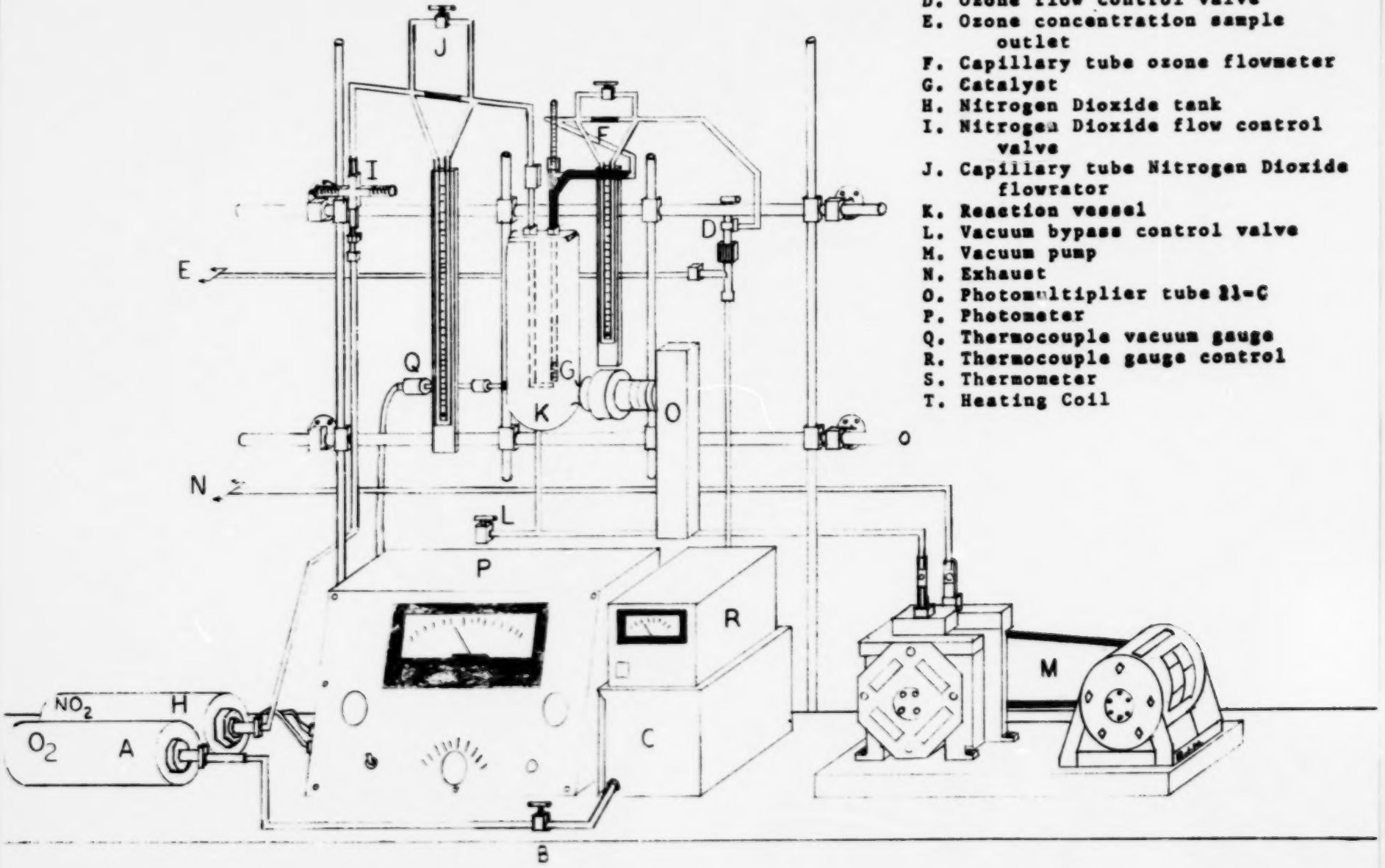


FIGURE I
INITIAL EXPERIMENTAL APPARATUS

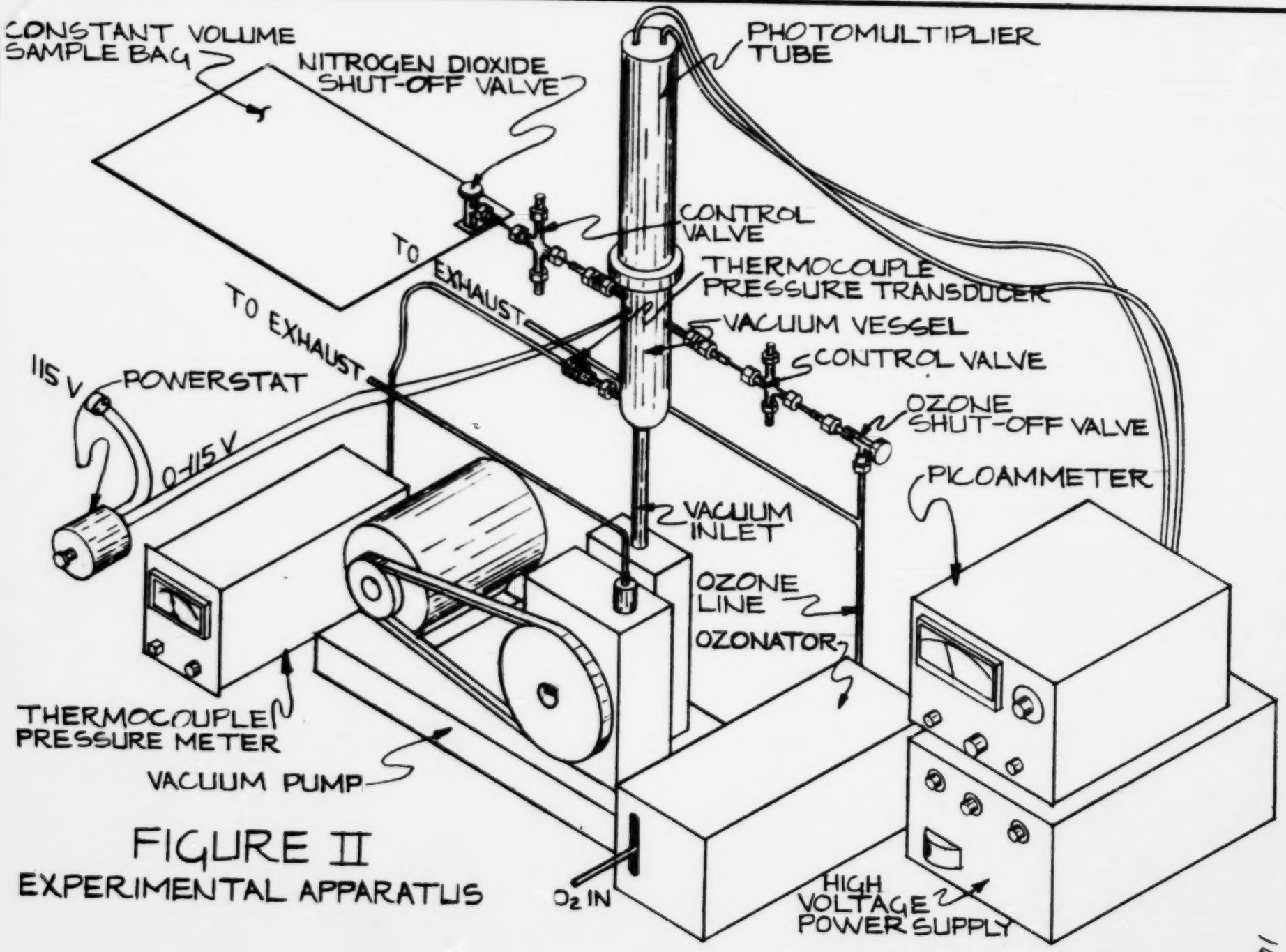


FIGURE II
EXPERIMENTAL APPARATUS

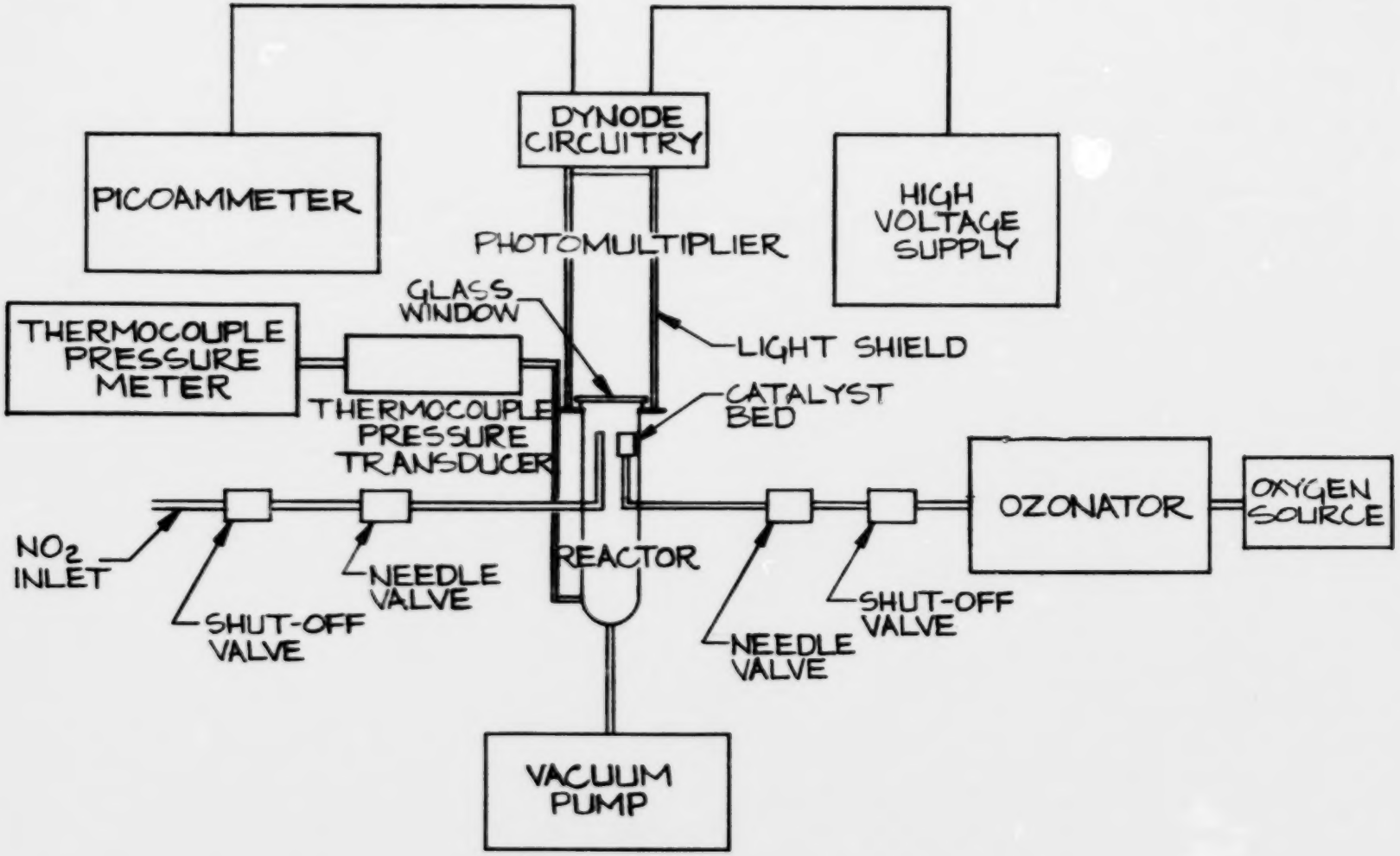
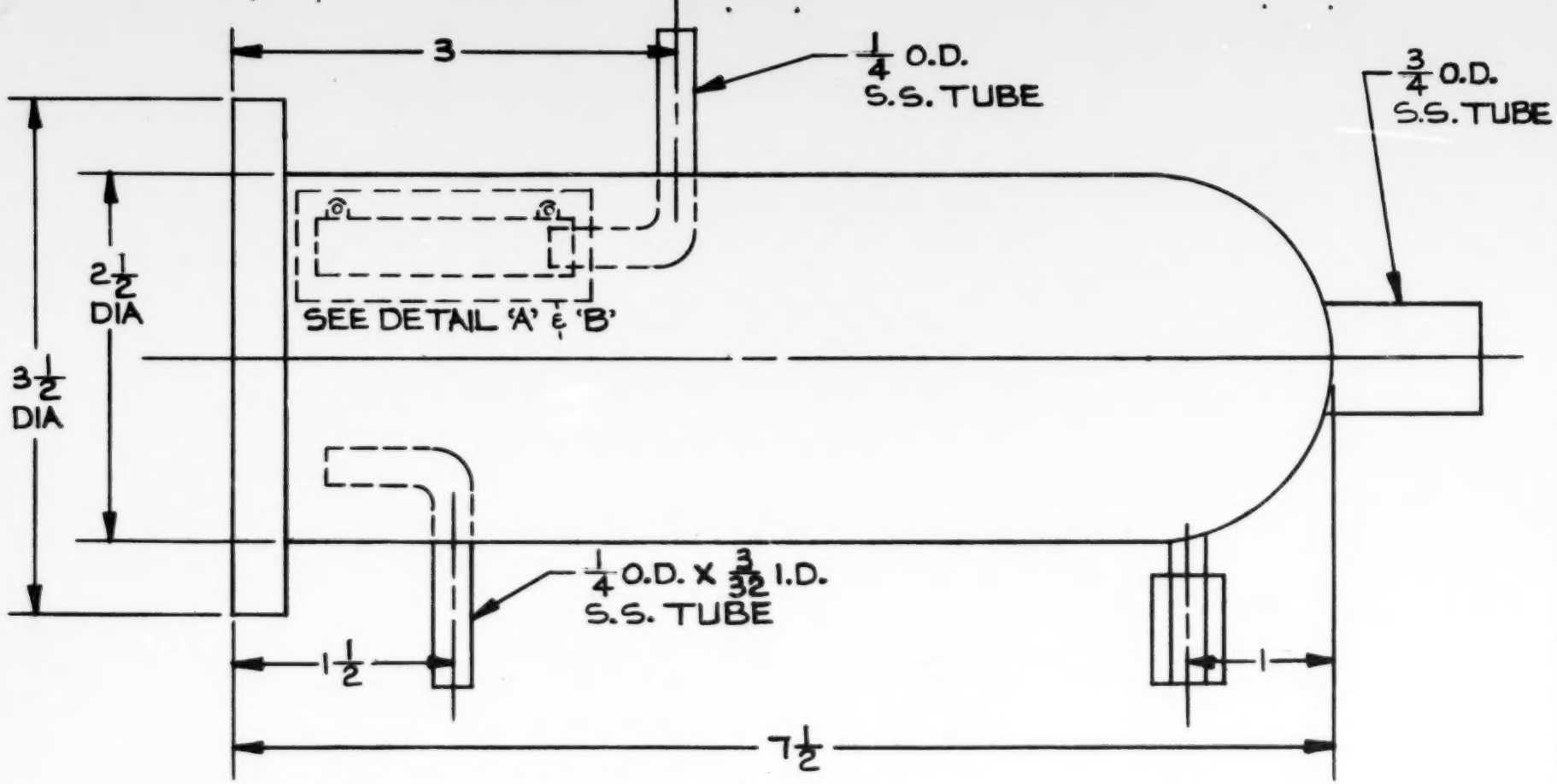
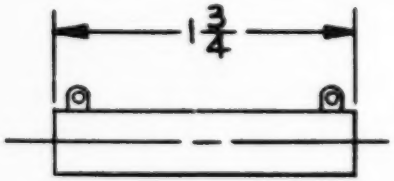
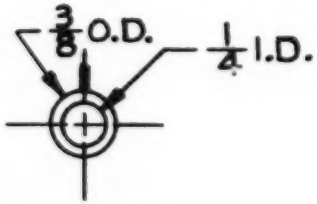


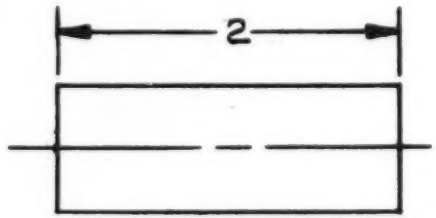
FIGURE III - BLOCK DIAGRAM

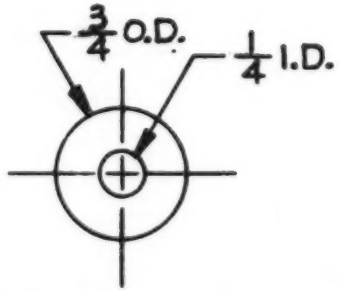






DETAIL 'A'
CERAMIC CATALYTIC CHAMBER
200 Ω 12 WATT RESISTOR





DETAIL 'B'
TEFLON CATALYTIC
CHAMBER

FIGURE IV-REACTION VESSEL